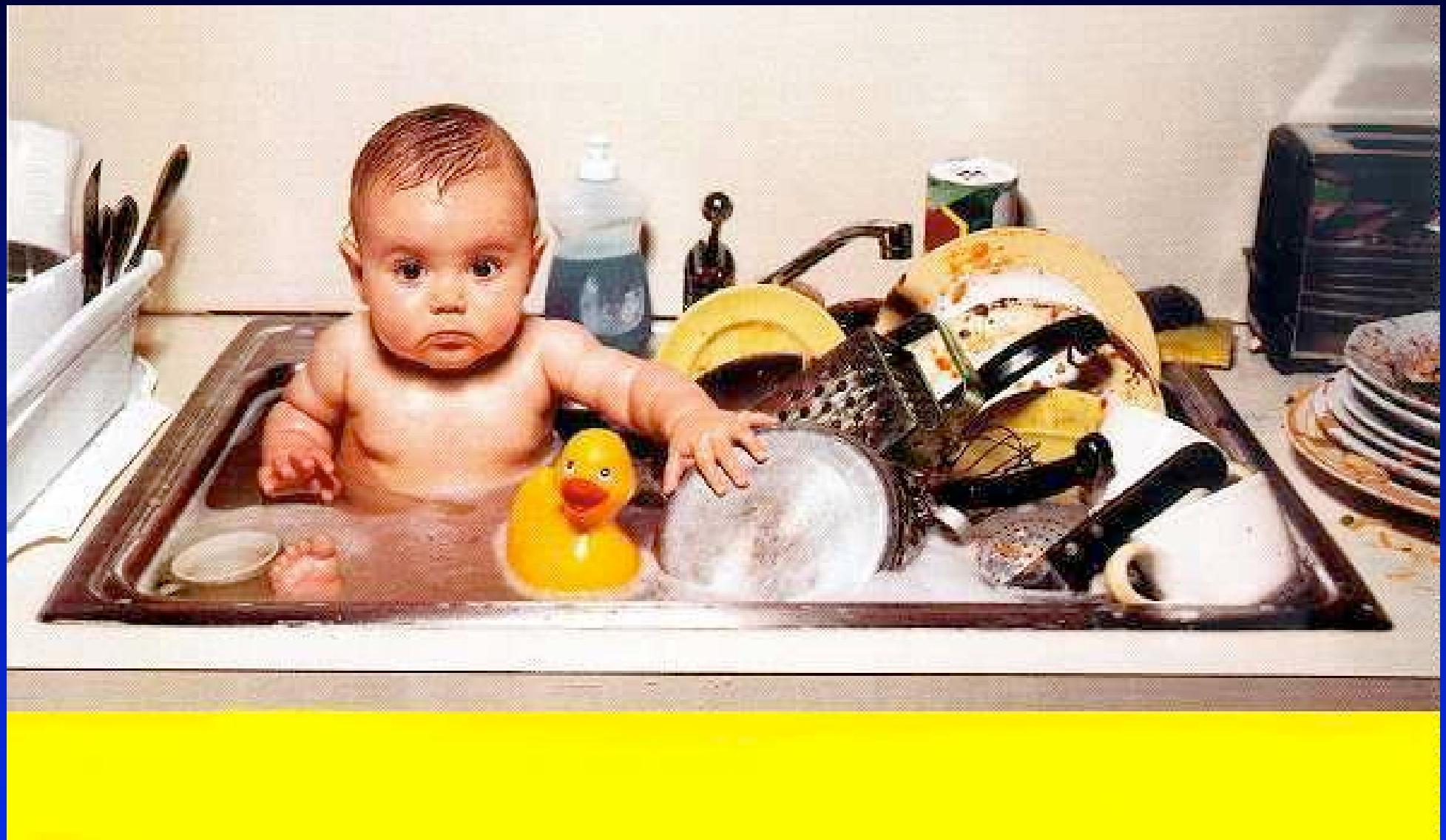
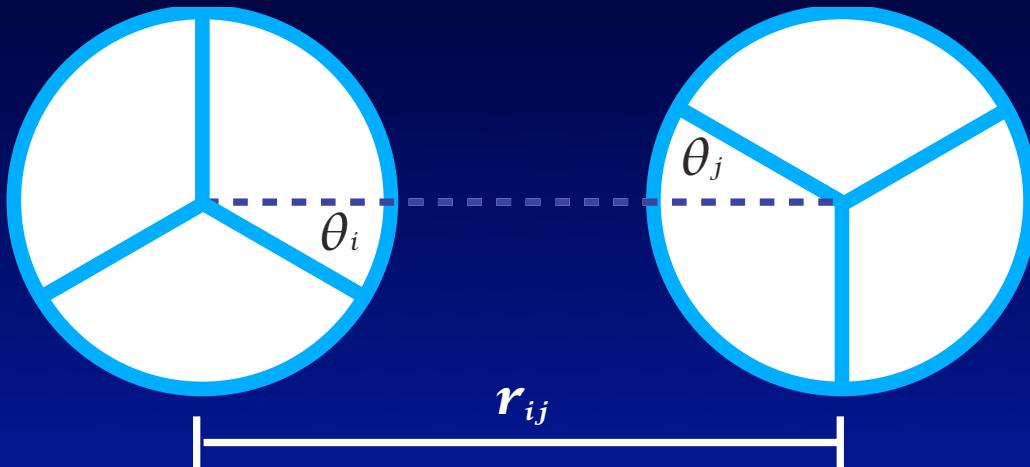


Modelling Water





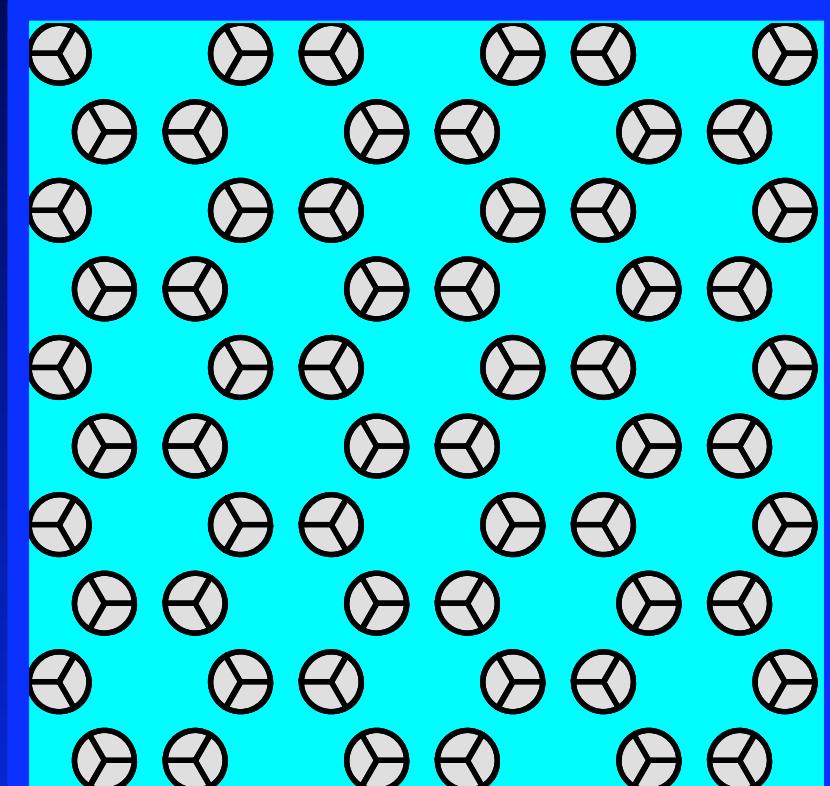
Mercedes Benz-ene



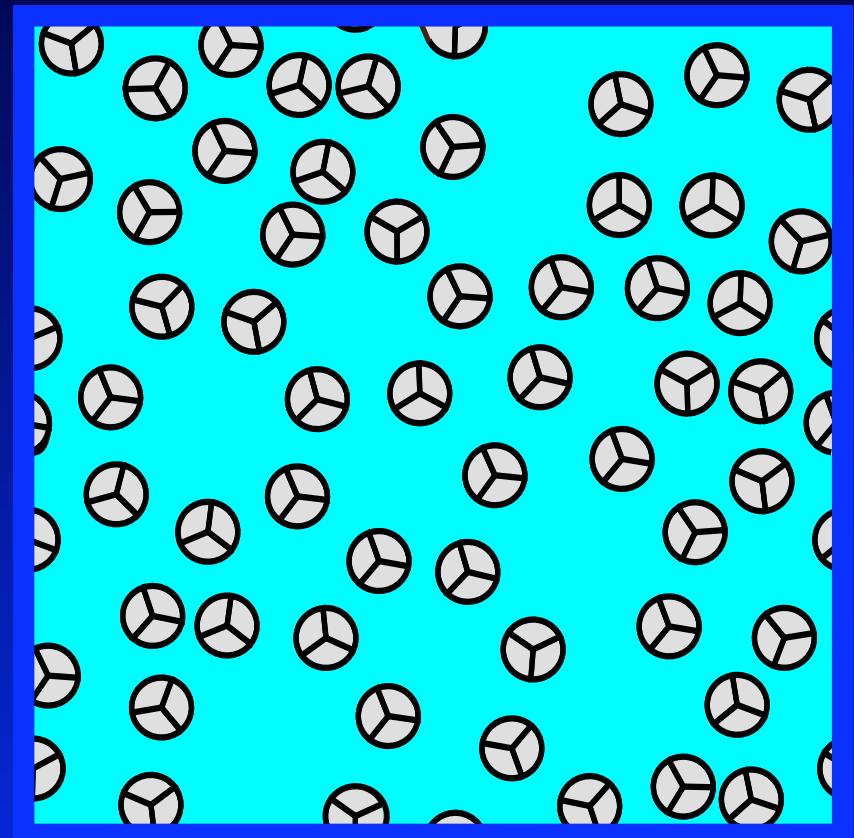
- $u(r) \approx (a/r)^{12} - (b/r)^6$
- H bond = Gaussian
- NPT Monte Carlo
- Nonpolar solute:

K Silverstein, ADJ Haymet, K Dill, JACS 120: 3166-3175 (1998)
A Ben Naim, J. Chem. Phys. 54: 3682 (1971)

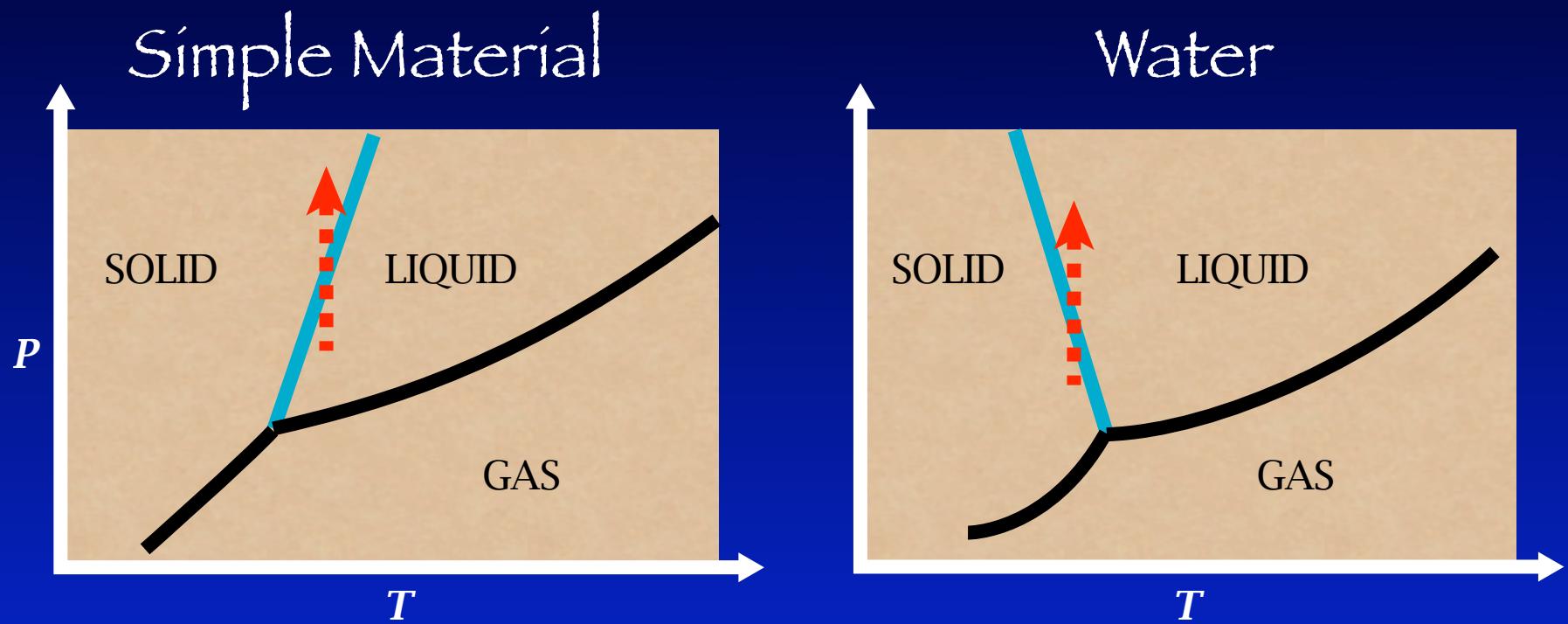
MB ‘Ice’



MB ‘Líquid’



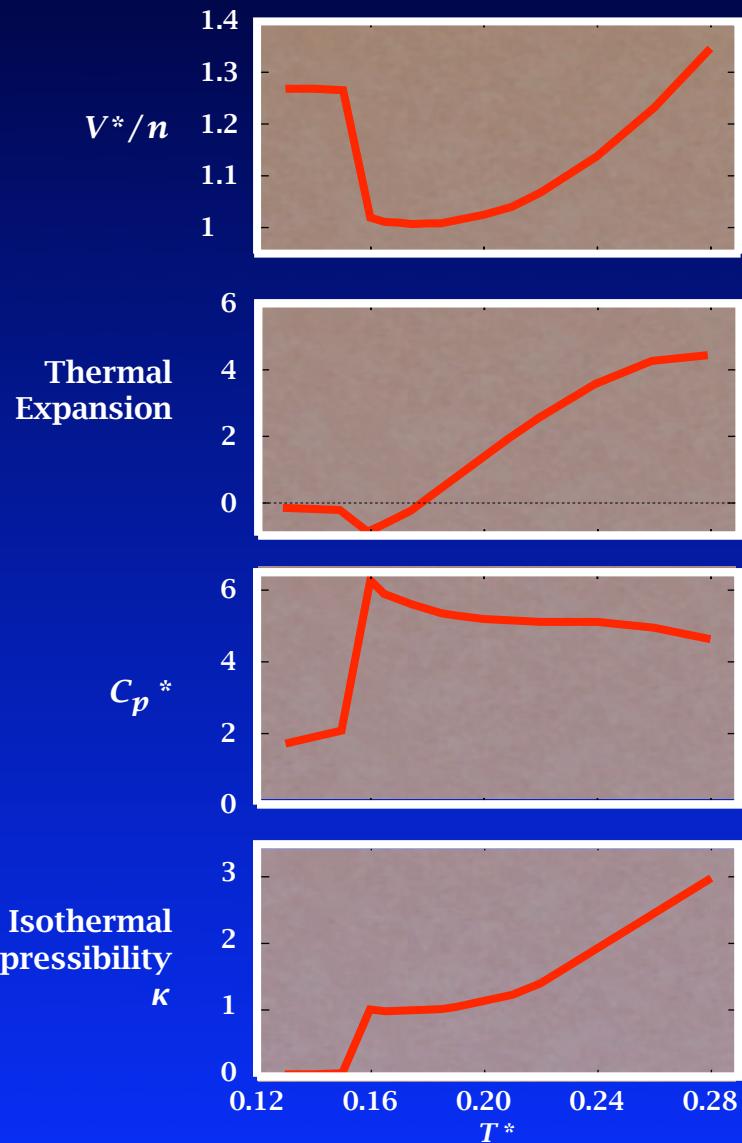
Pressure Melts MB Ice



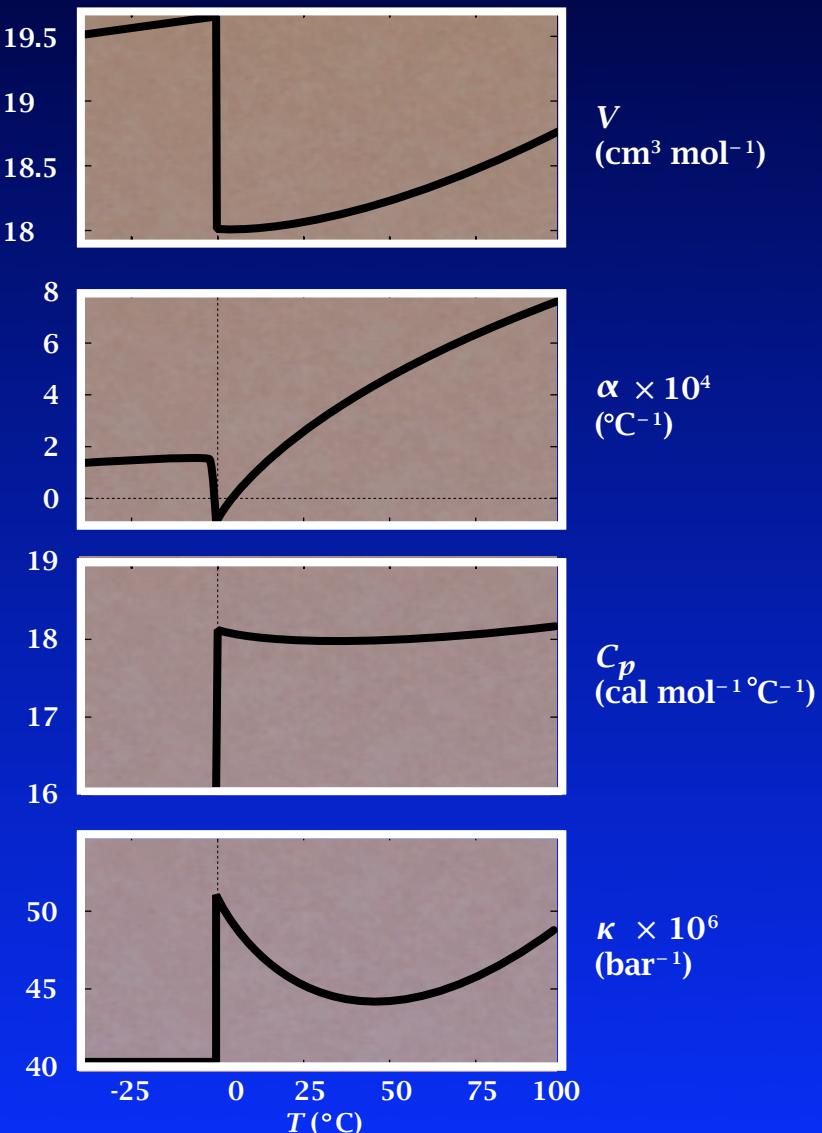
Clapeyron Relation
 $\frac{\partial S}{\partial V} < 0 \Rightarrow \frac{\partial P}{\partial T} < 0$

Anomalous Properties of Water

MB Model

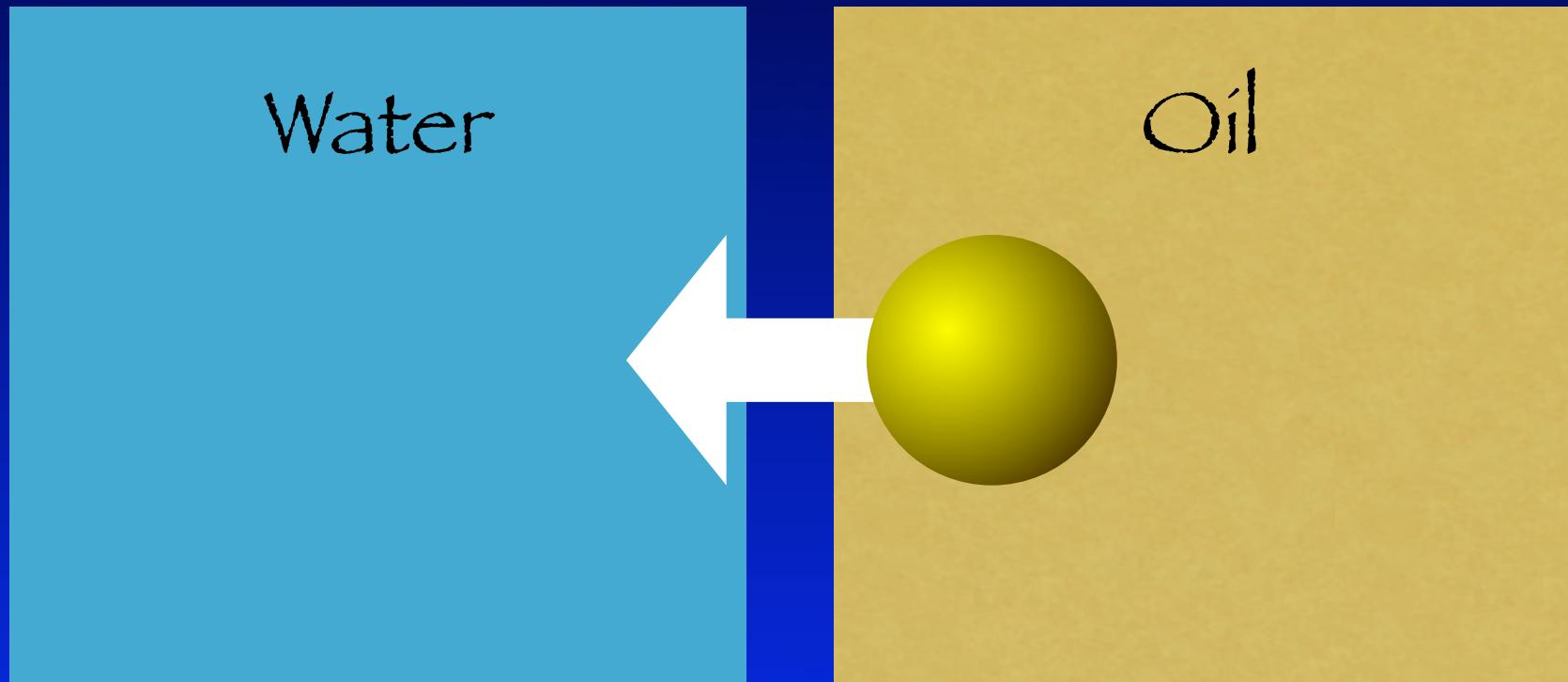


Experiments



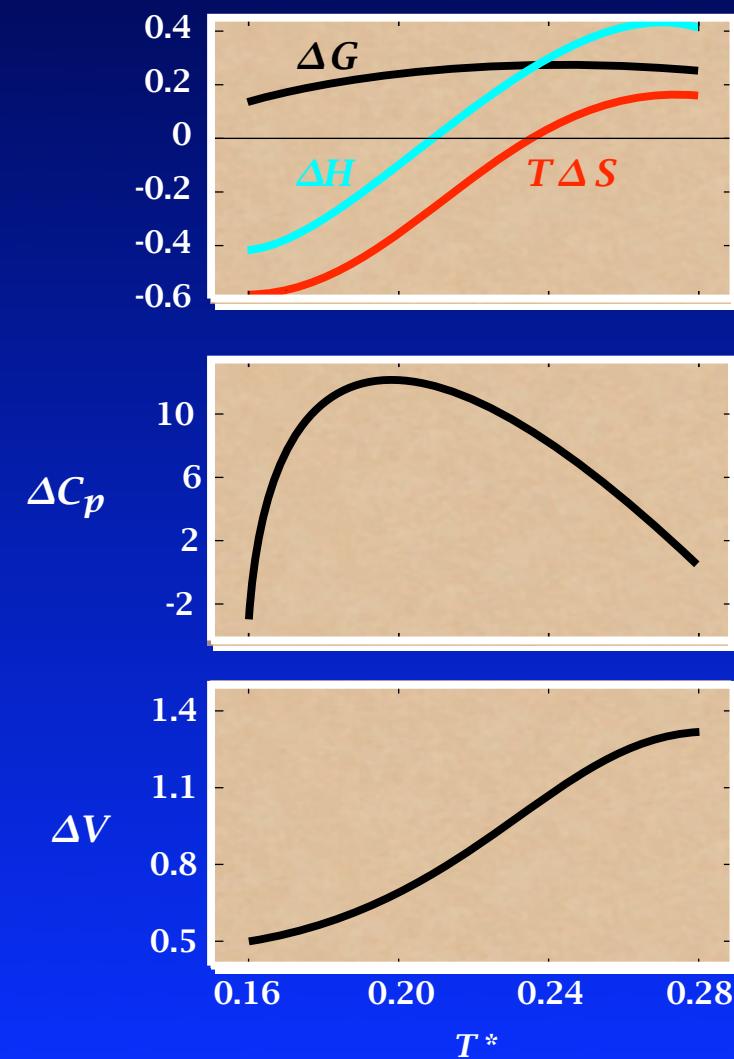
The Hydrophobic Effect

Thermal Behavior of Nonpolar Transfers

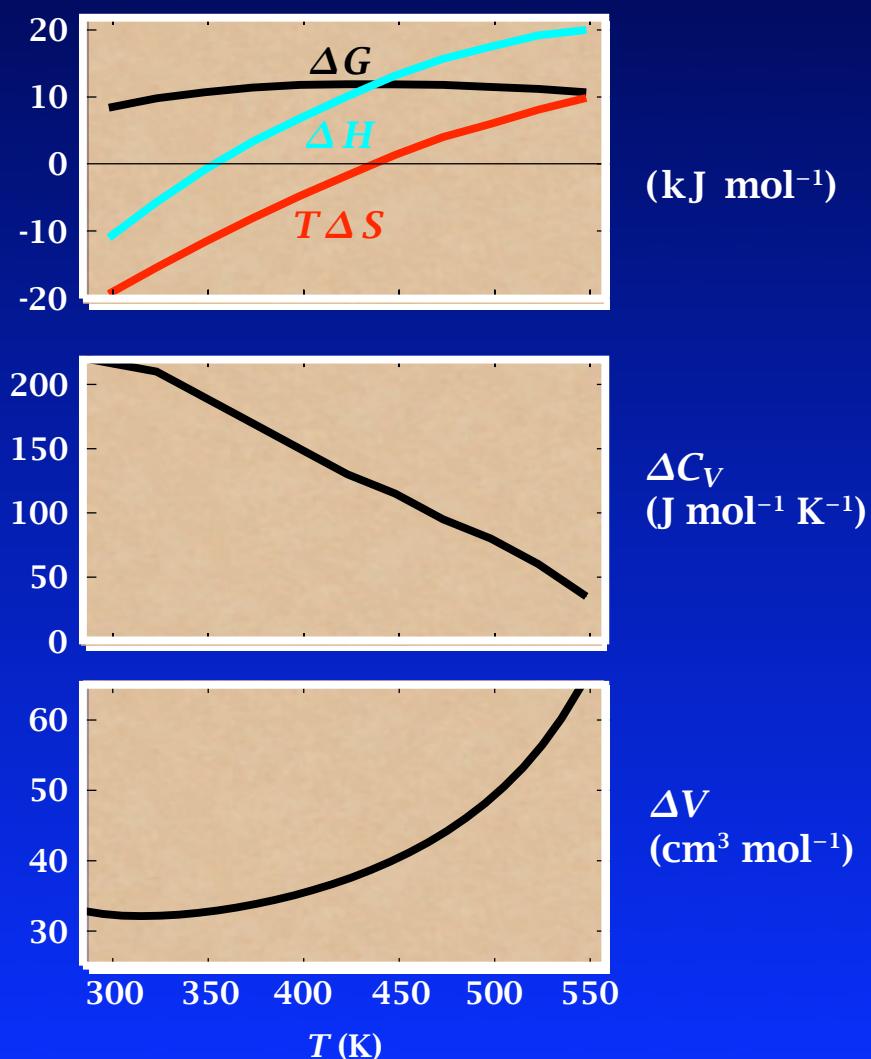


Hydrophobicity: Temperature Dependence

MB Model

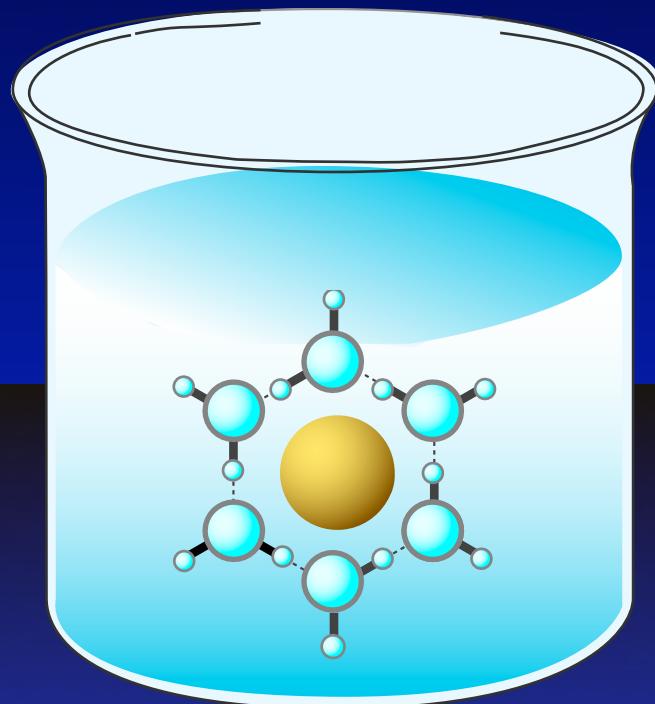


Experiments

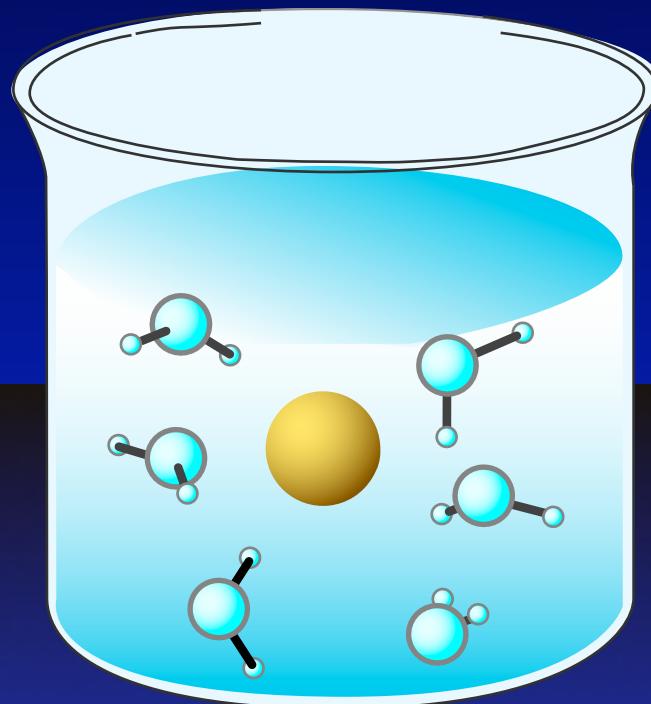


Hydrophobic Heat Capacity

Cold Water



Hot Water



Solute Orders Water

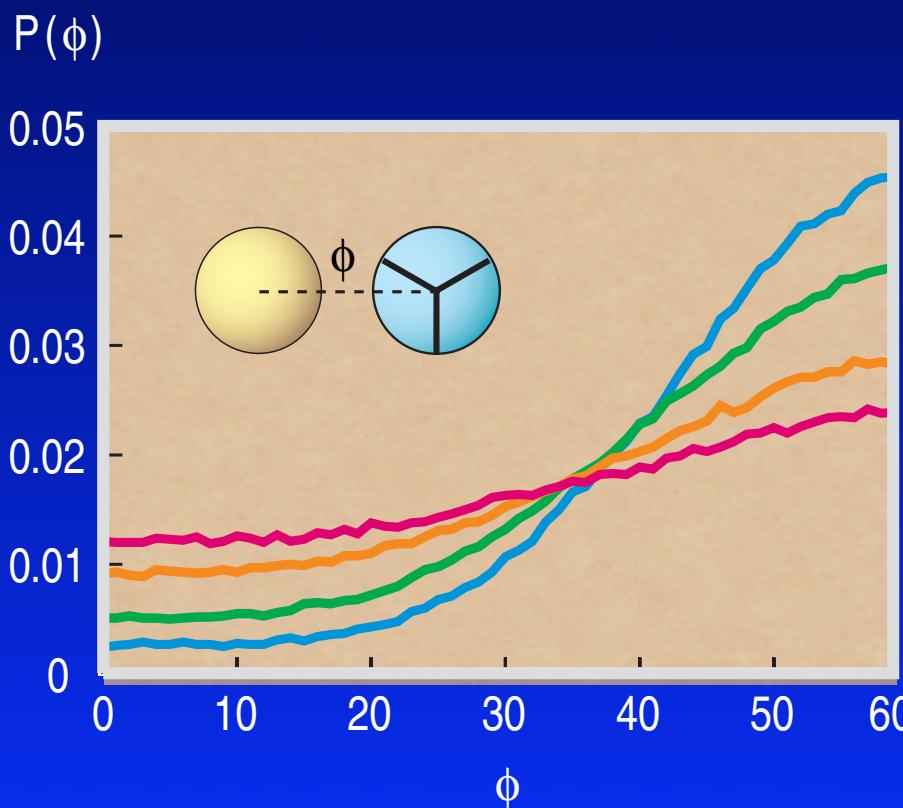
$$-T\Delta S \gg 0$$

Solute Disorders Water

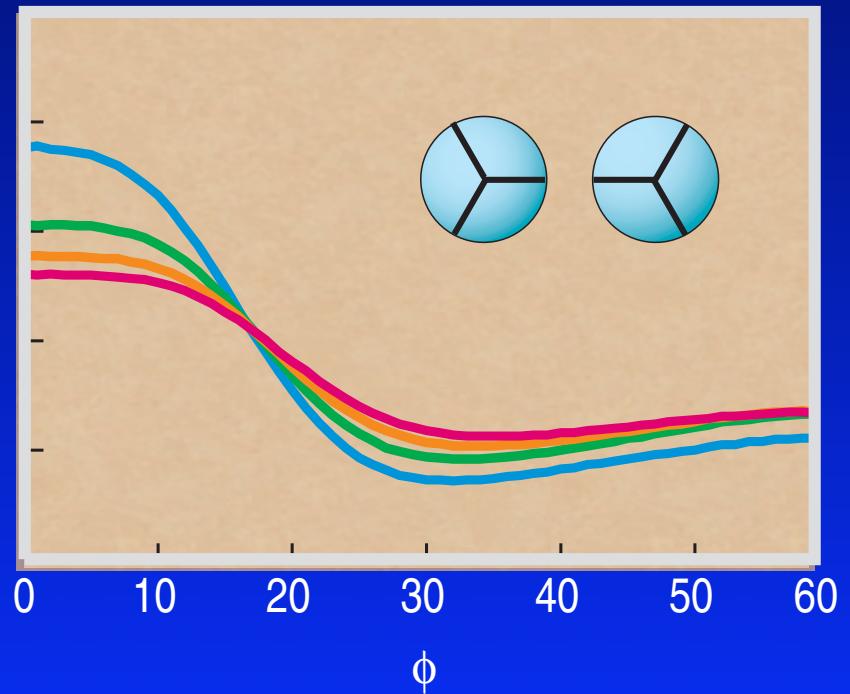
$$\Delta H \gg 0$$

Orientational Preferences Decrease with Temperature

Solute-Water

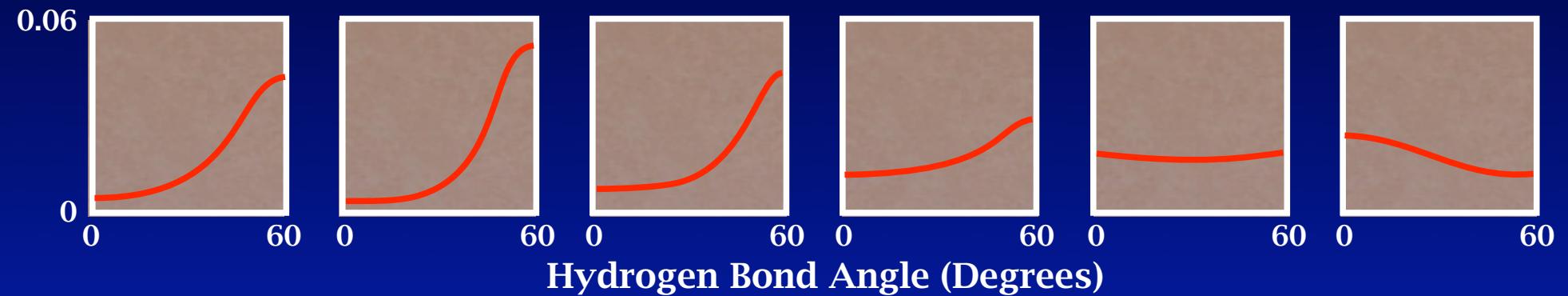


Water-Water

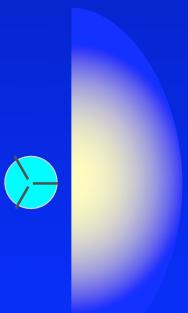
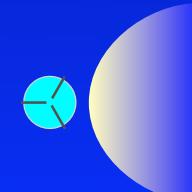
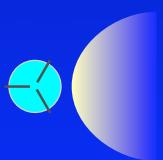
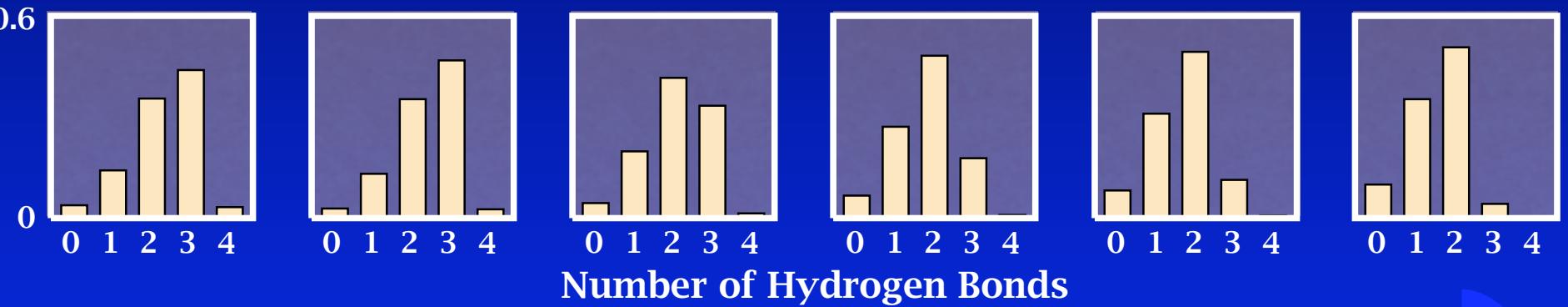


First-Shell Water Orientations Depend on Solute Size

Fraction

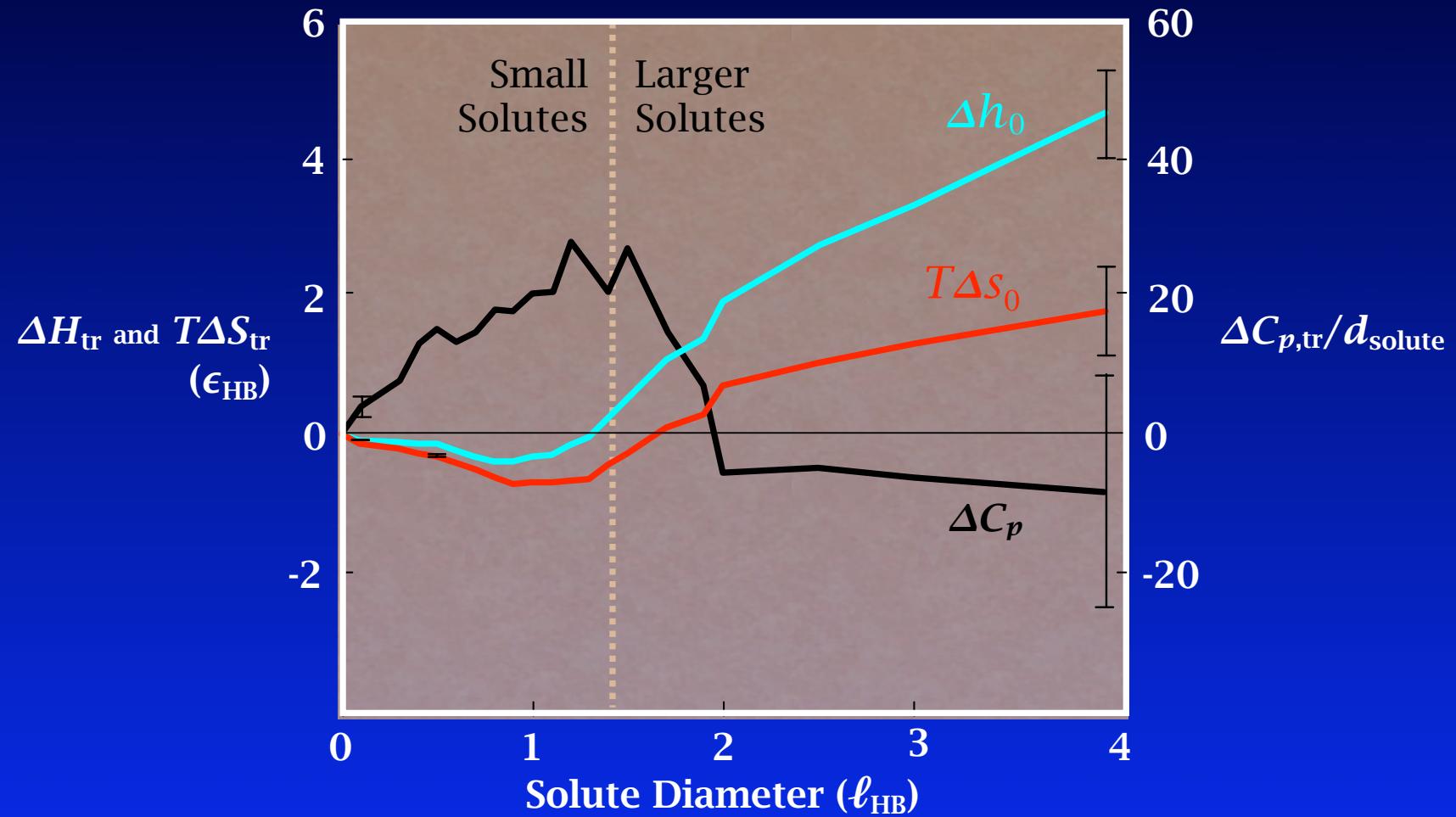


Fraction

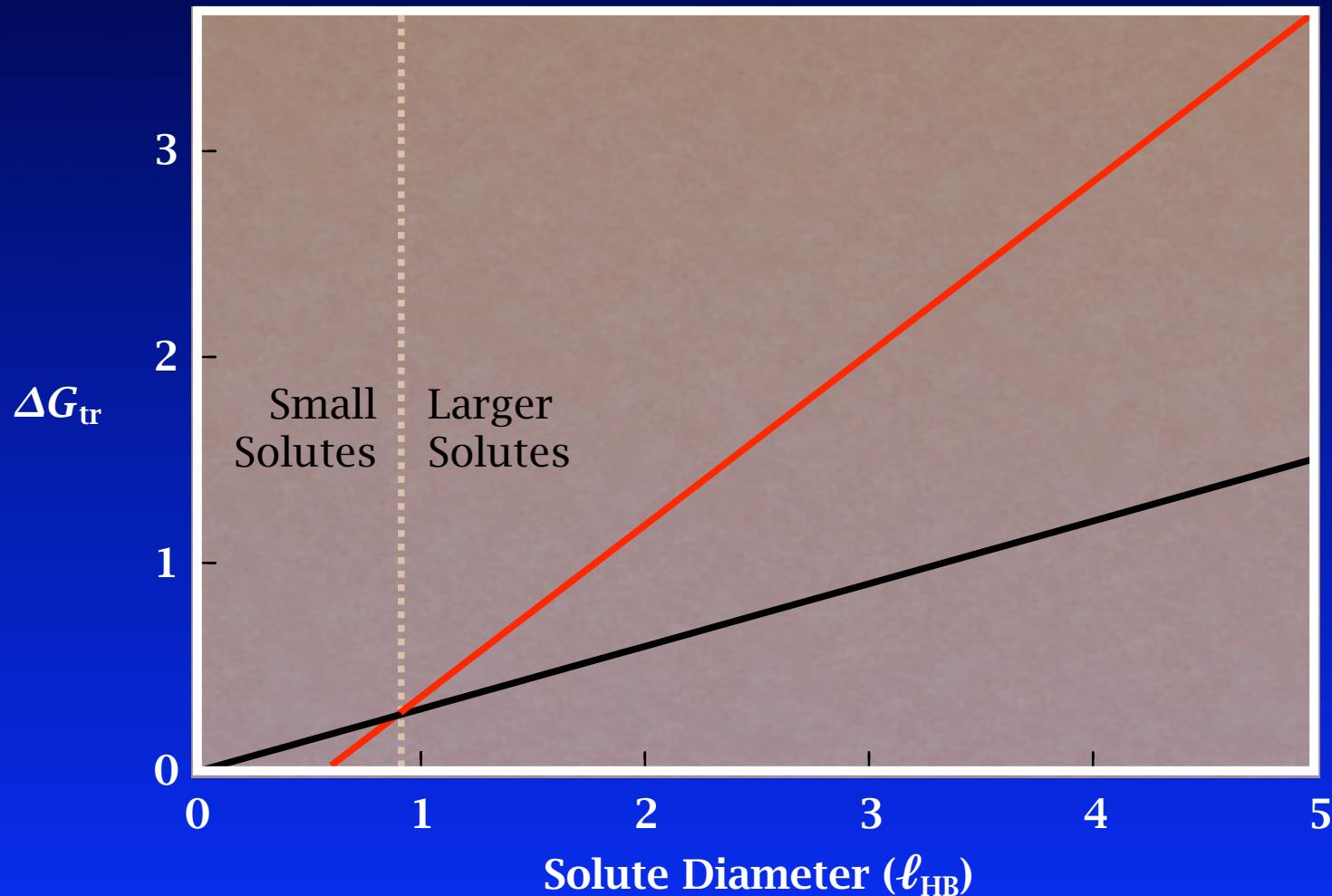


Hydrophobic Solutes

Properties Differ: Large vs. Small



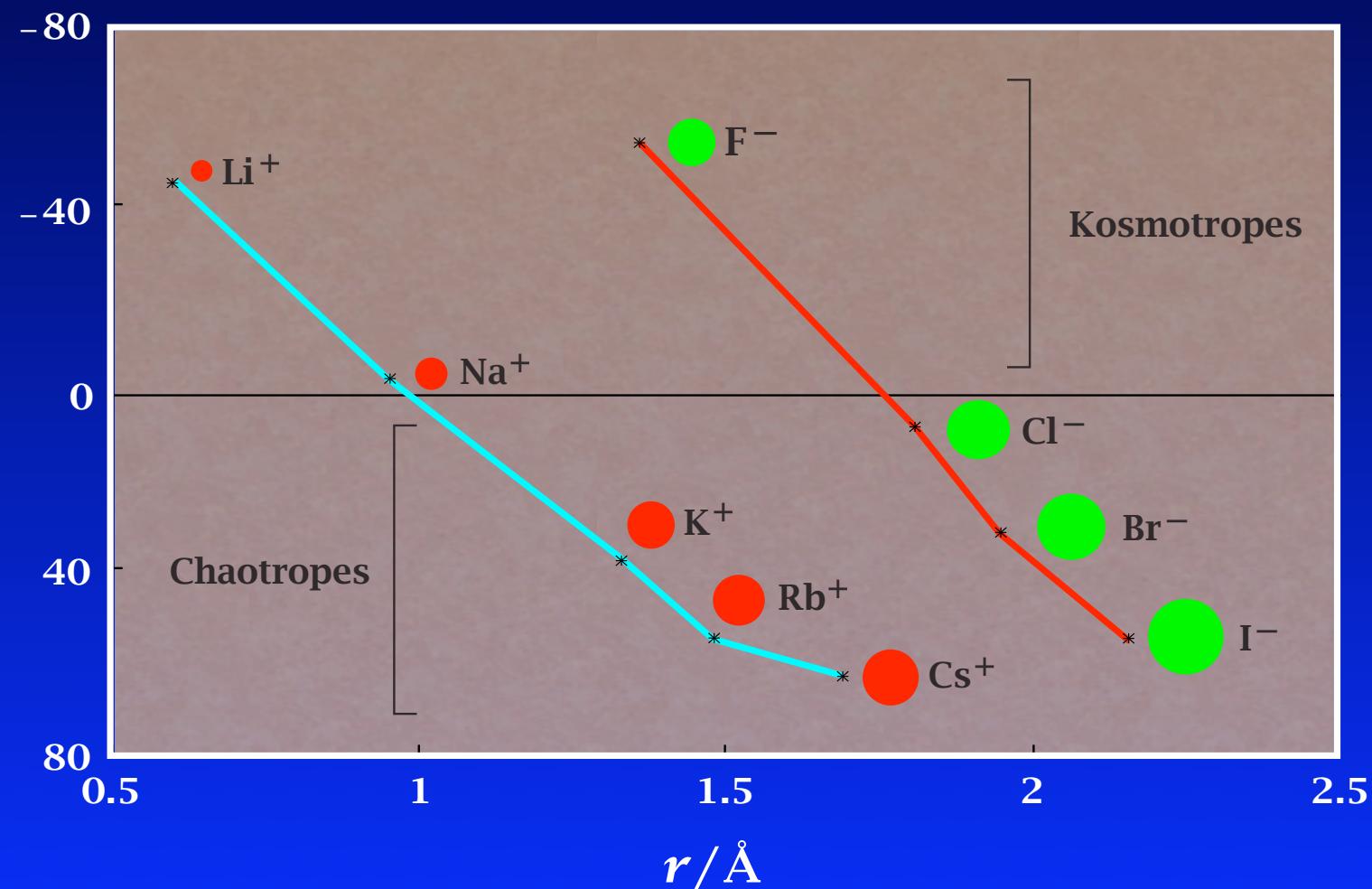
Free Energy of Transfer: Mechanism Changes with Solute Size



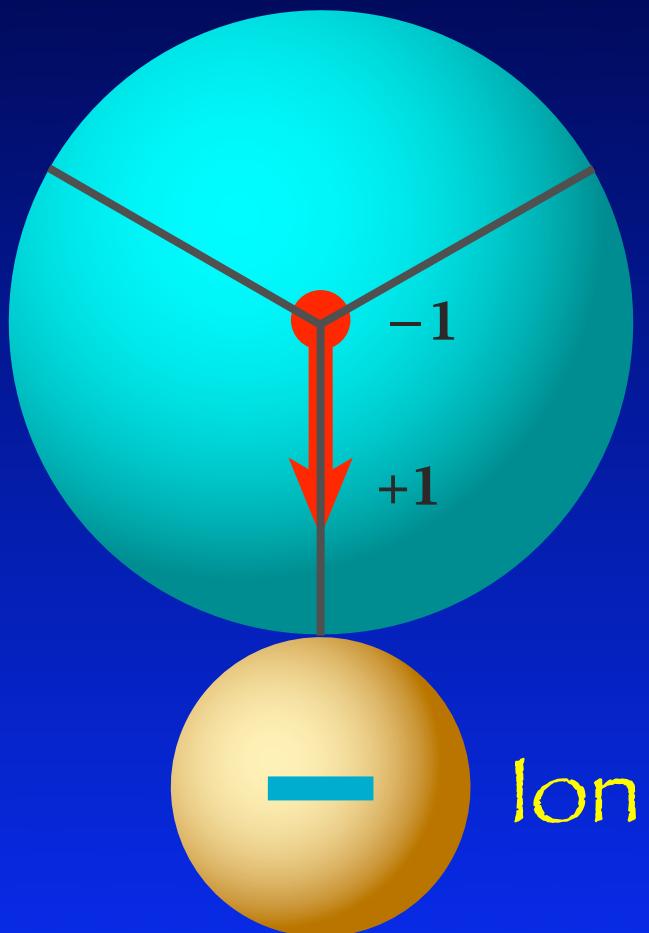
Small Ions Order Water.

Large Ions Disorder Water.

$\Delta S / \text{J mol}^{-1} \text{K}^{-1}$

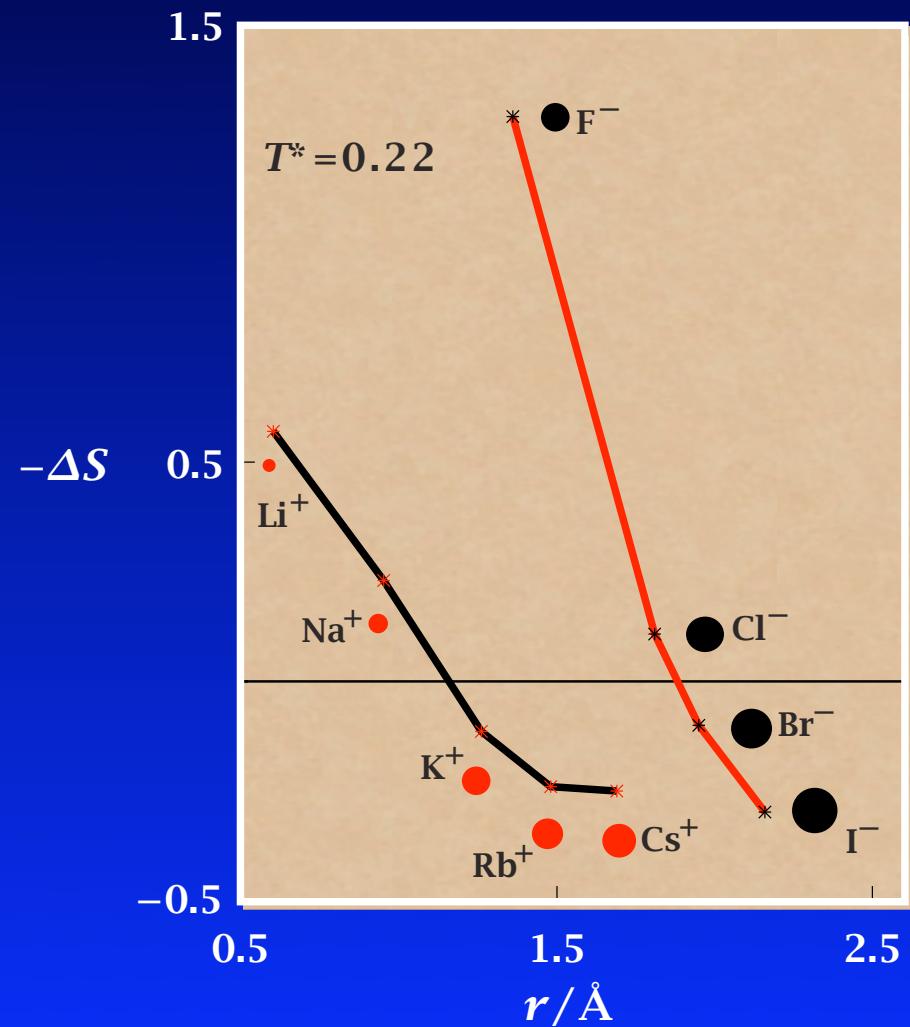


MB + Dipole Water Model for Ion Solvation

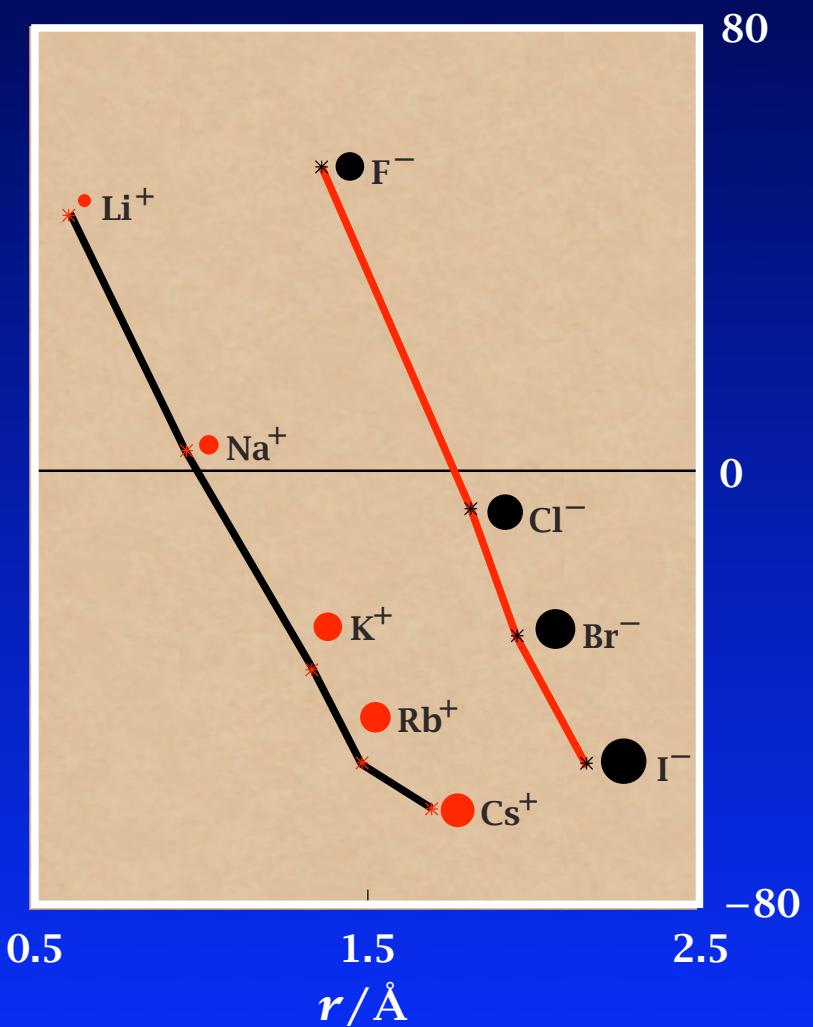


Chaotropes & Kosmotropes

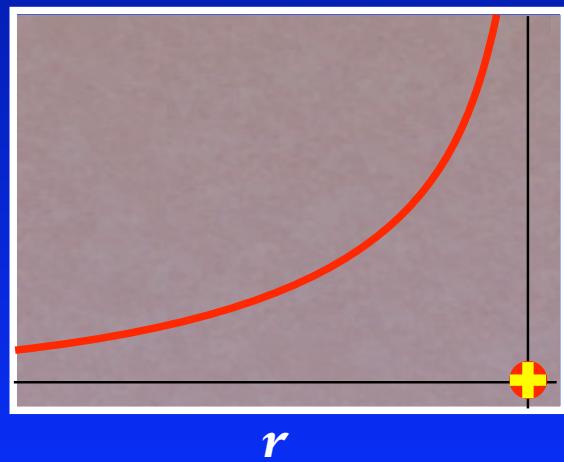
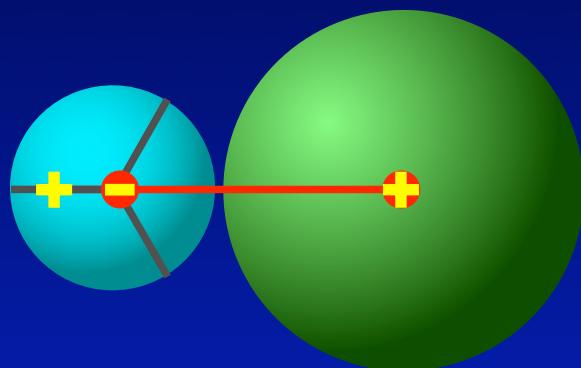
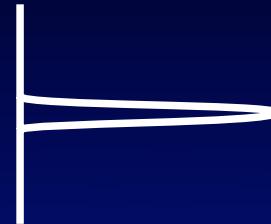
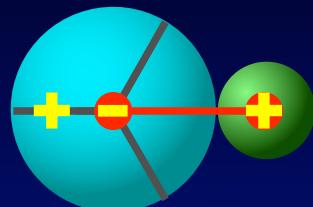
Theory



Experiment

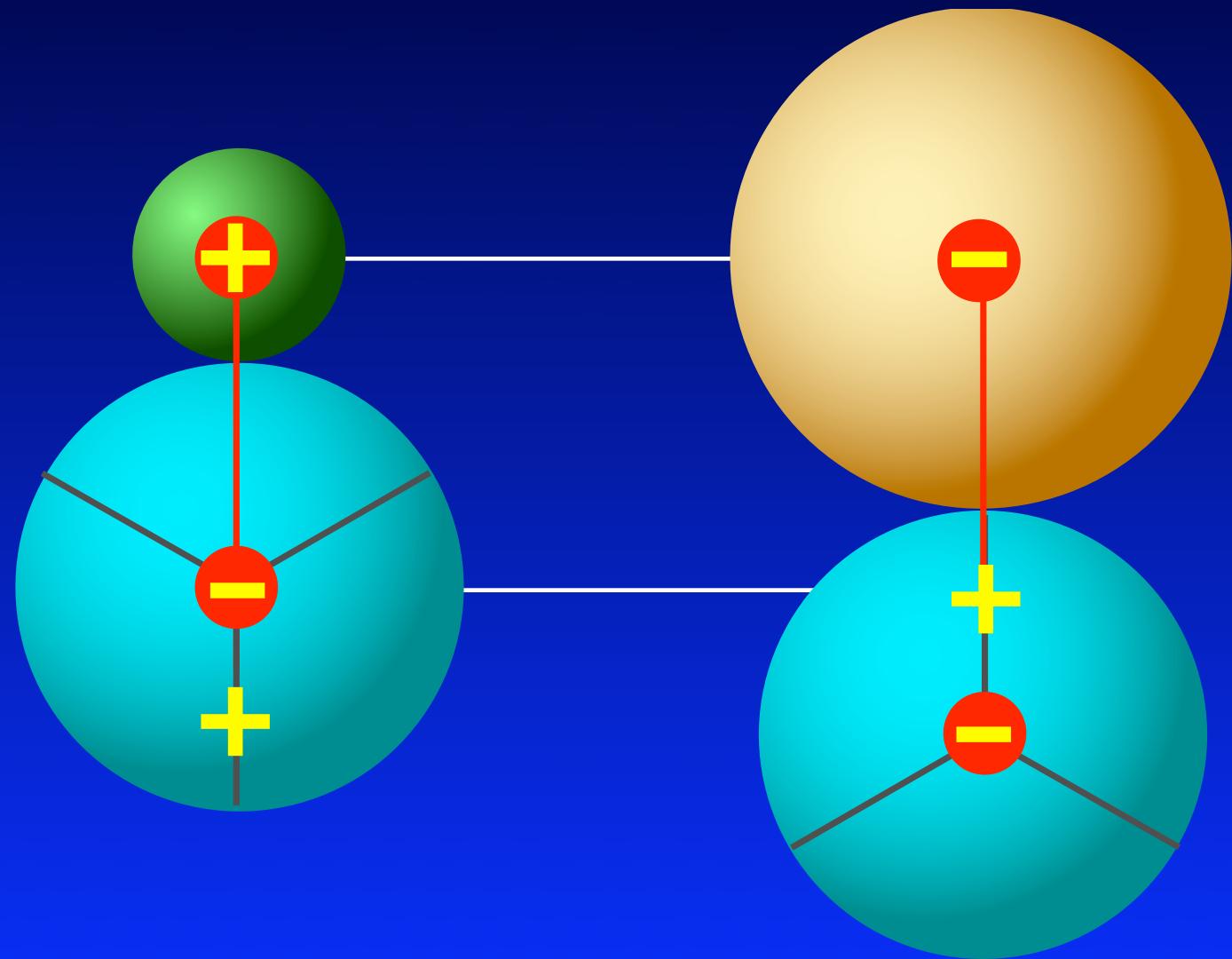


Small Ions Order Water



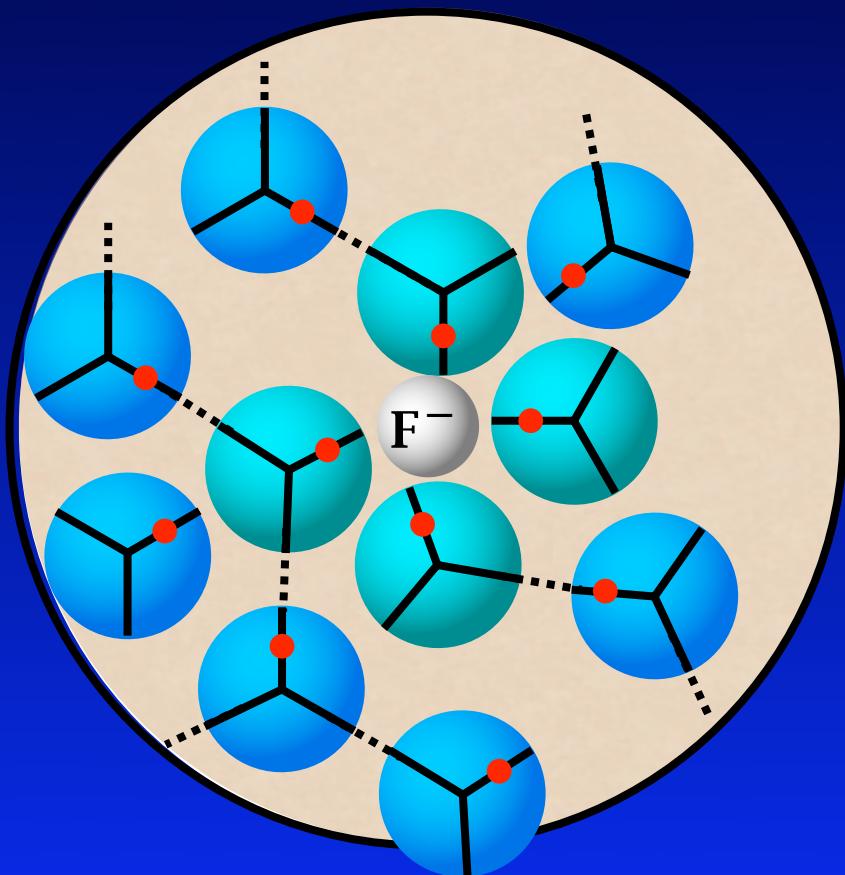
Electrostatic
Potential
 $\psi(r)$

Small Cations & Large Anions

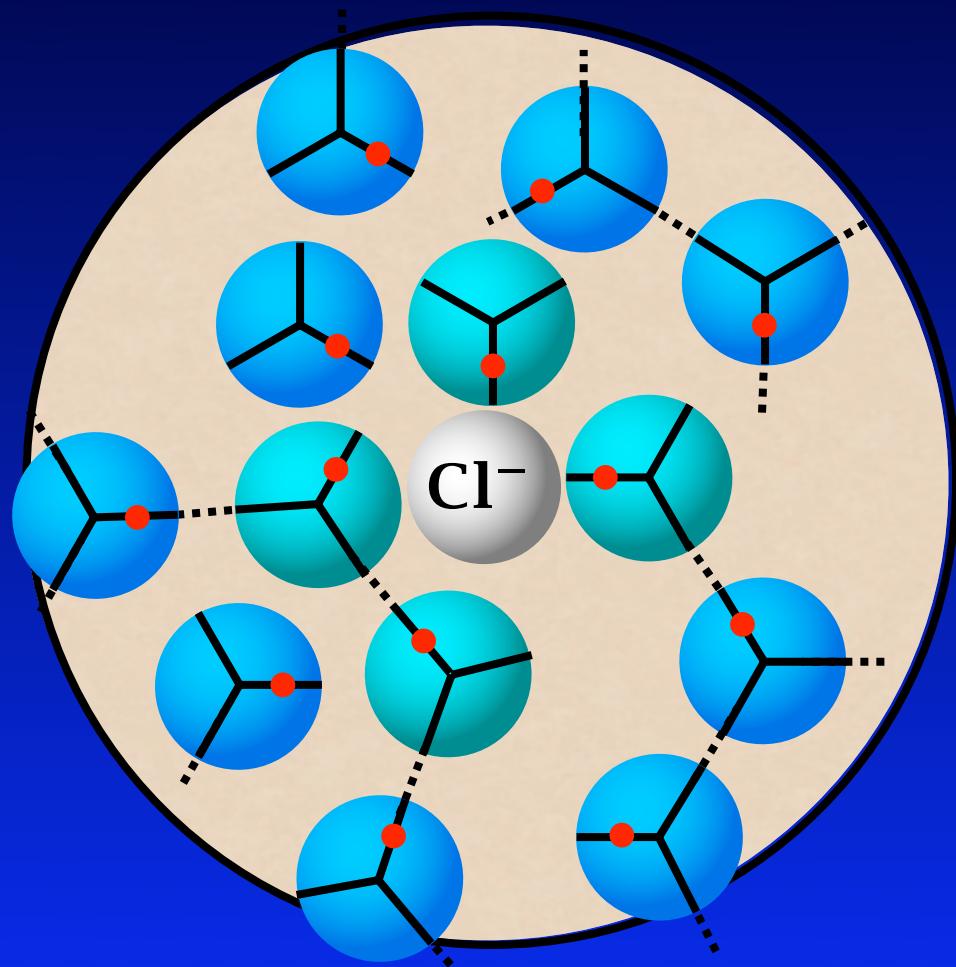


Water Around Ions

Electrostatic Ordering Around Small Ions

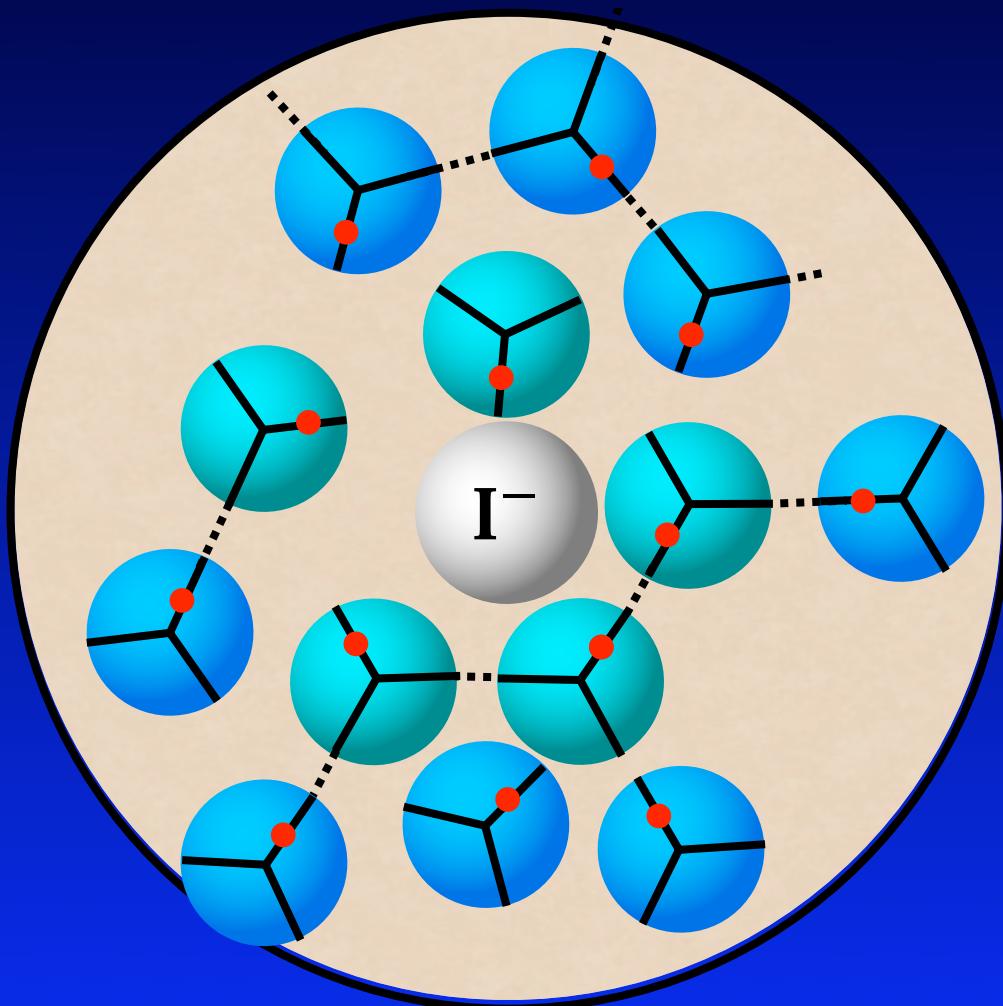


Water Around Ions



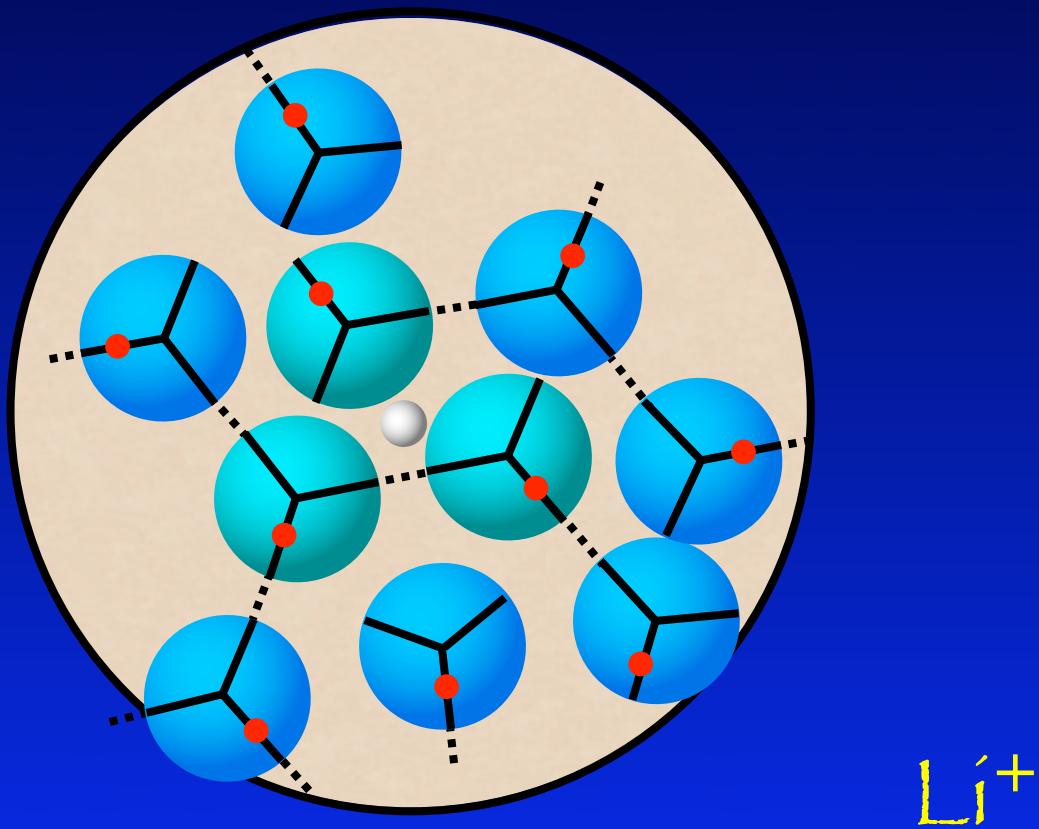
Water Around Ions

Hydrophobic Ordering Around Large Ions

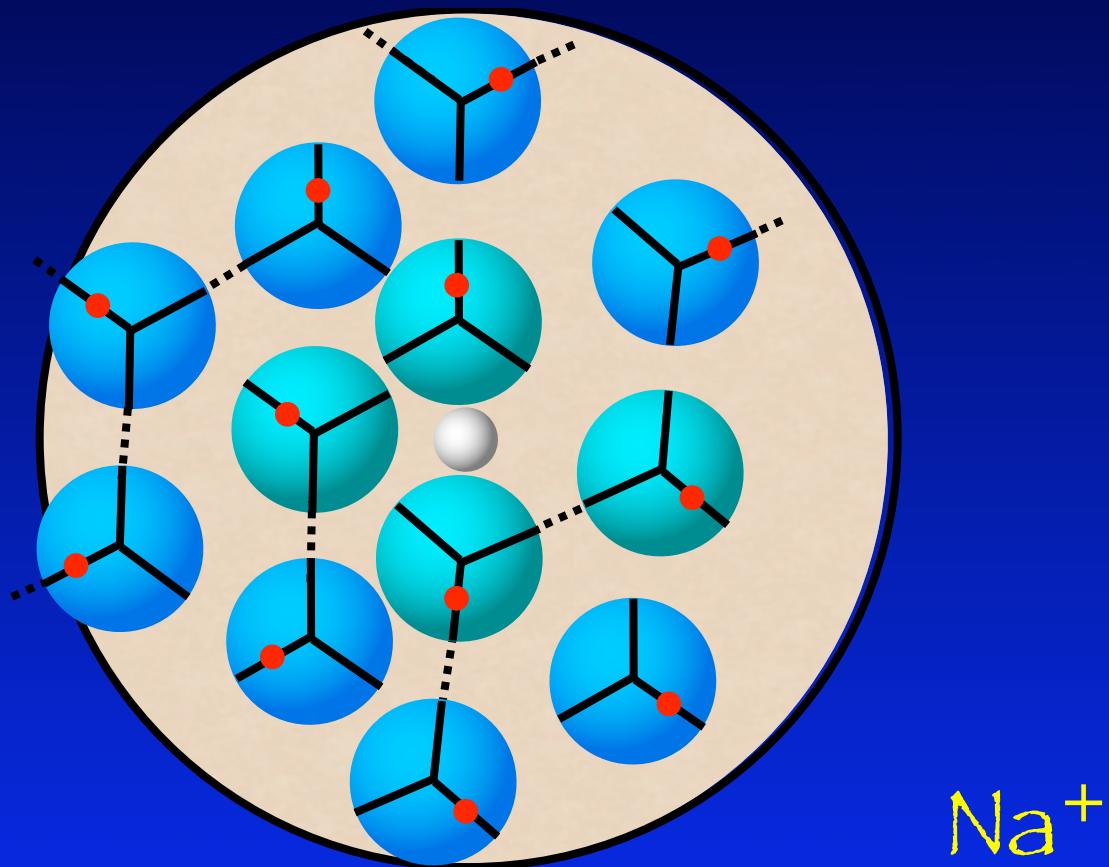


Water Around Ions

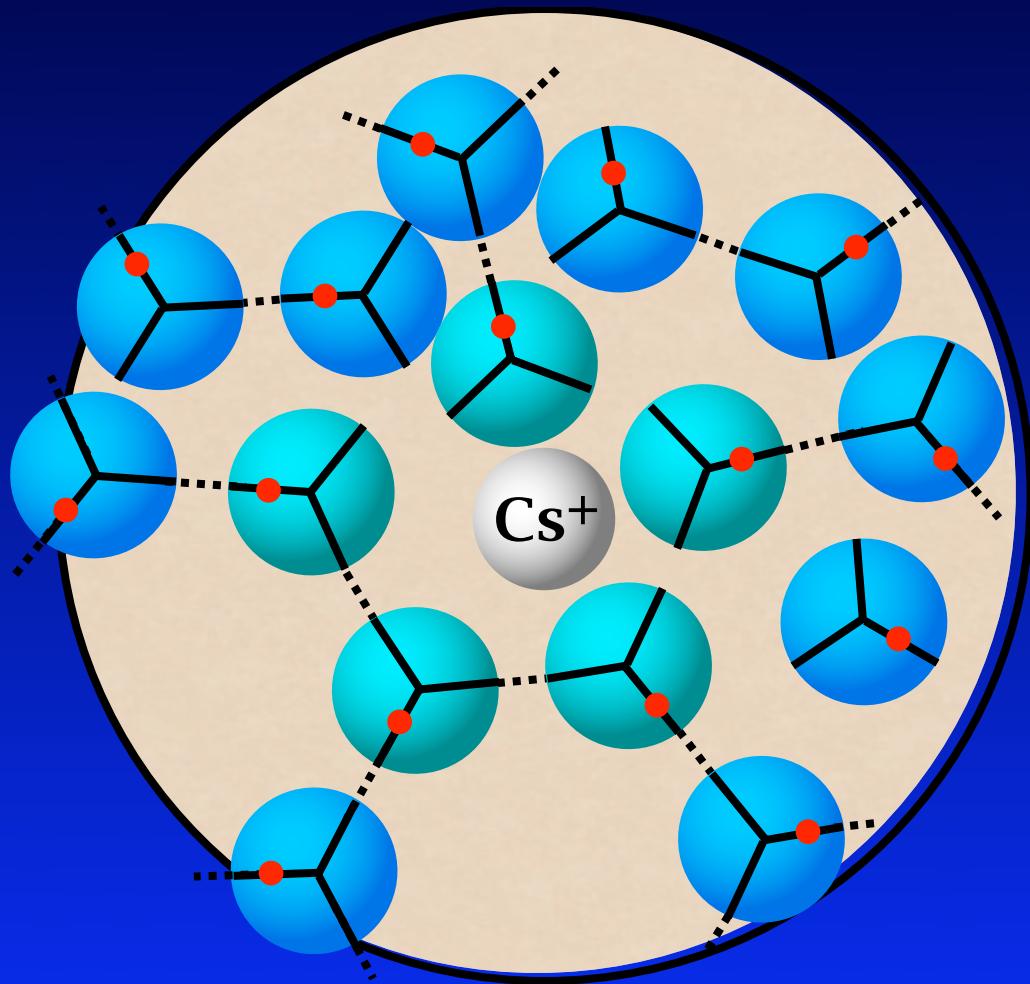
Electrostatic Ordering Around Small Ions



Water Around Ions

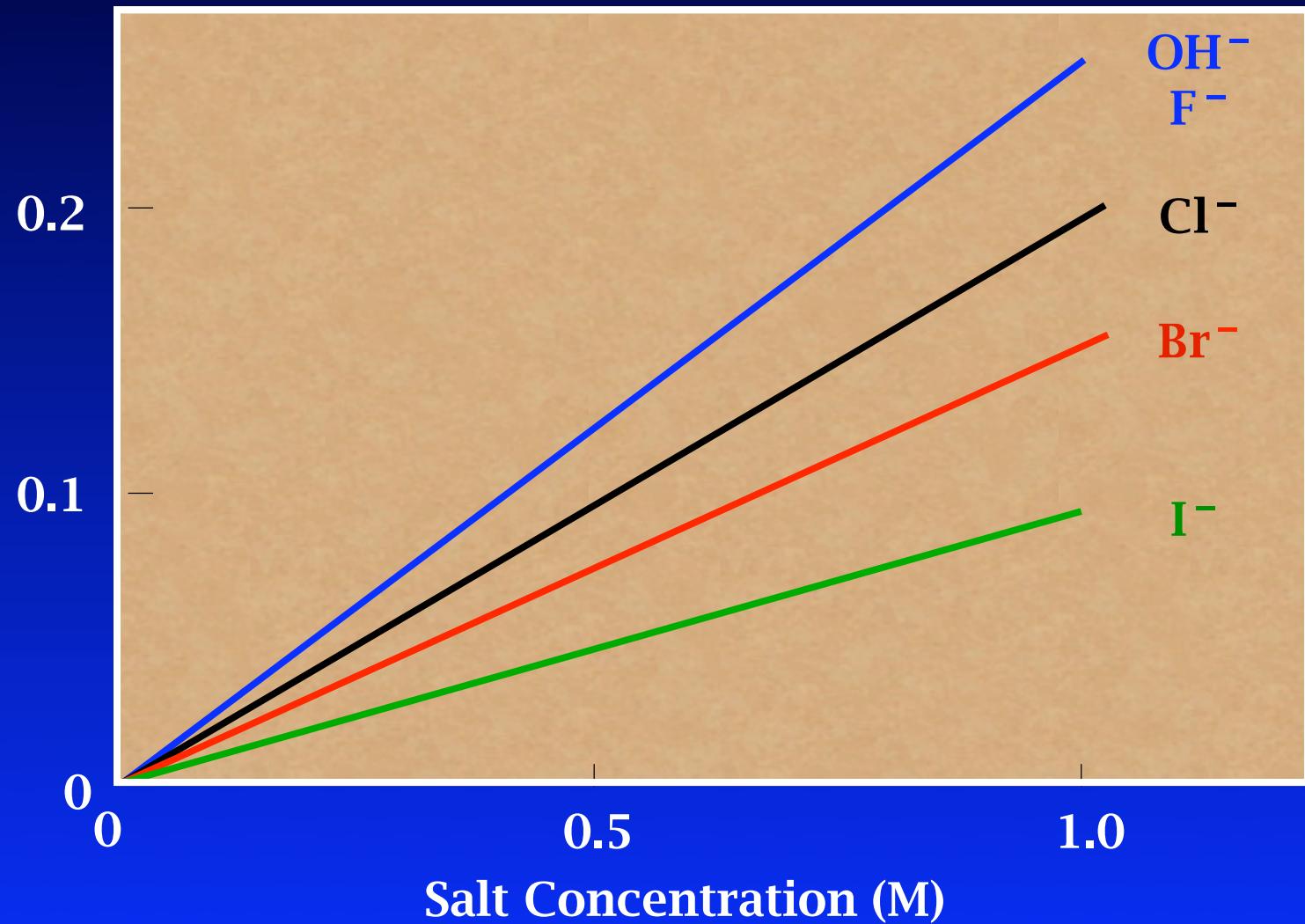


Water Around Ions



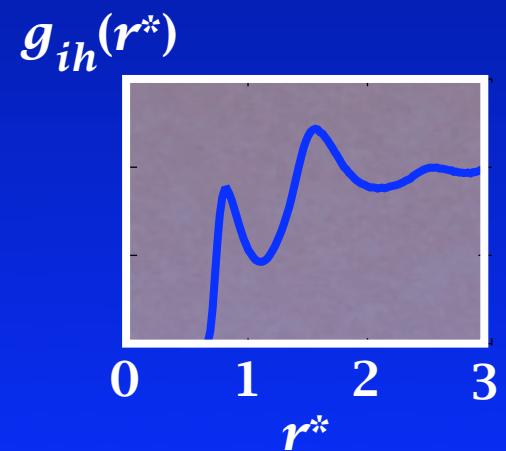
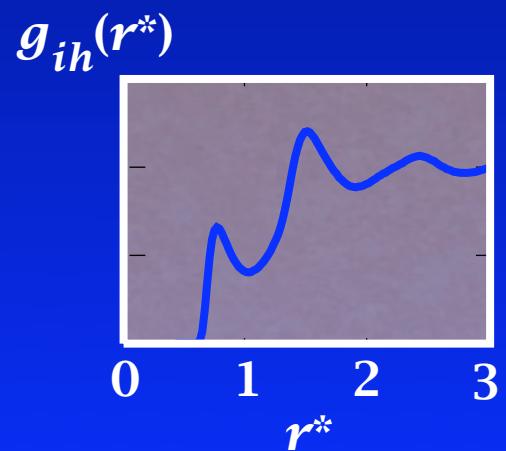
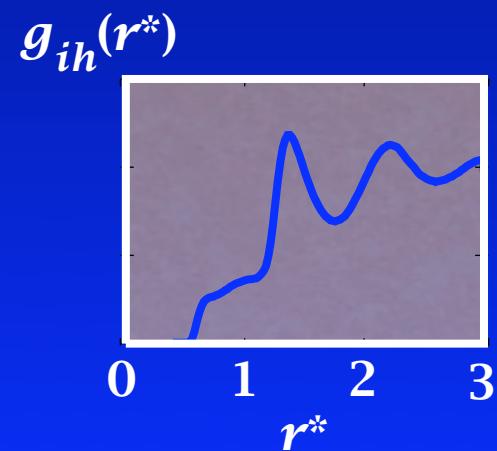
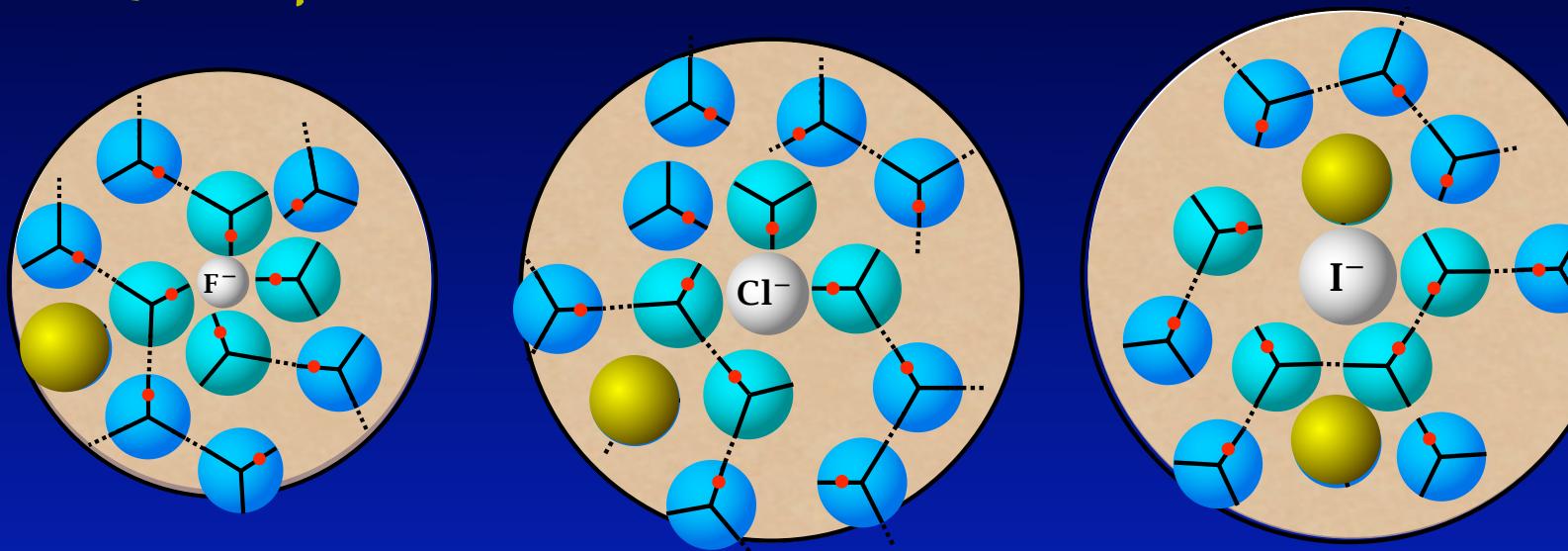
The Hofmeister Series of Ions

-Log (Relative Solubility)



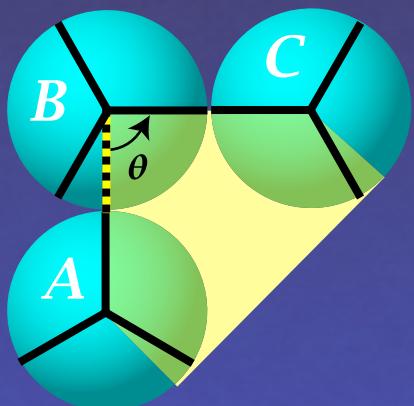
Hofmeister Effect:

Hydrophobes Excluded from Ion Shell



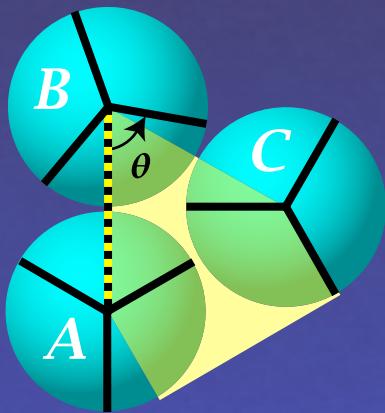
3-State 3-Water (3S3W) Model

Cagelike



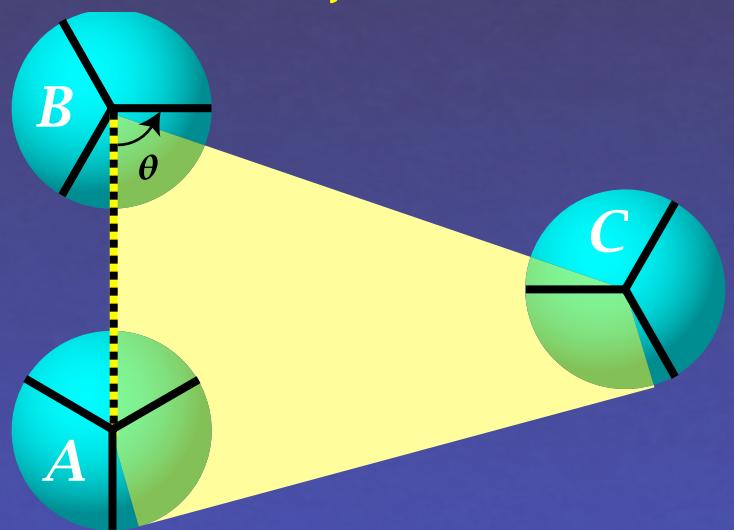
$$u_1 = -\epsilon_{HB} + k_s \theta^2$$

Dense



$$u_2 = -\epsilon_D$$

Open



$$u_3 = 0$$

Partition Function

$$\Delta = \frac{(\Delta_{\text{cell}})^N}{N!}$$

$$\Delta_{\text{cell}} = \sum_{j=1}^3 \exp[-\beta P v_j] \int \int \int dx_B dy_B d\theta \exp[-\beta u_j]$$

Partition Function

$$\Delta_{\text{cell}}(T, p, N) = 2\pi d^2 c(T) N \left\{ g_1 \alpha_1 e^{-\epsilon_{HB}/(kT)} + \alpha_2 e^{-\epsilon_D/(kT)} + g_3 \alpha_3 \right\}$$

$$g_1 = \sqrt{kT/(\pi k_s)} \operatorname{erf} \left(\sqrt{\pi^2 k_s / (9kT)} \right)$$

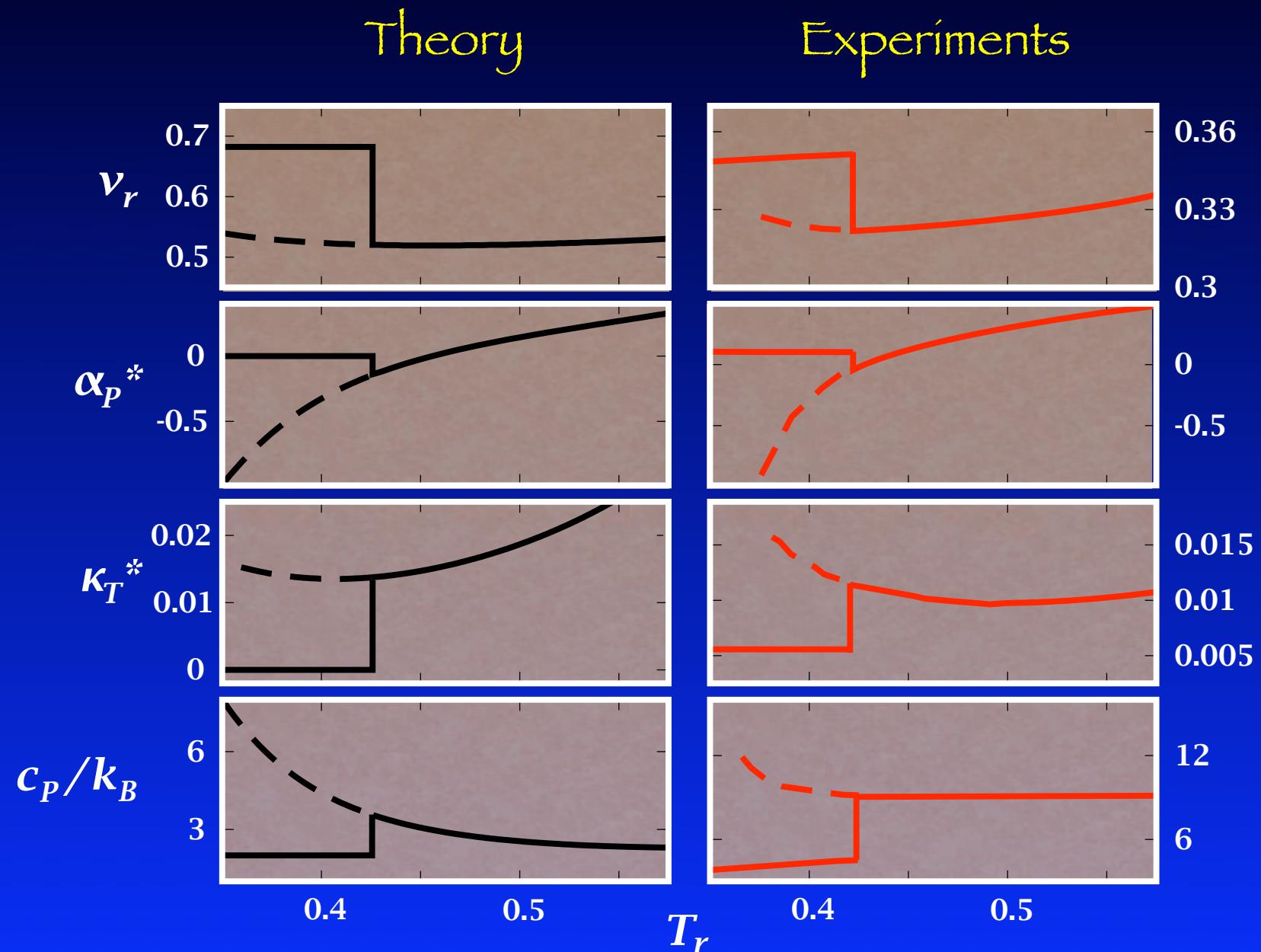
$$\alpha_1 = e^{[-p(3\sqrt{3}d^2/4)]/(kT)]}$$

$$\alpha_2 = e^{[-p(2+\sqrt{3})d^2/(4kT)]}$$

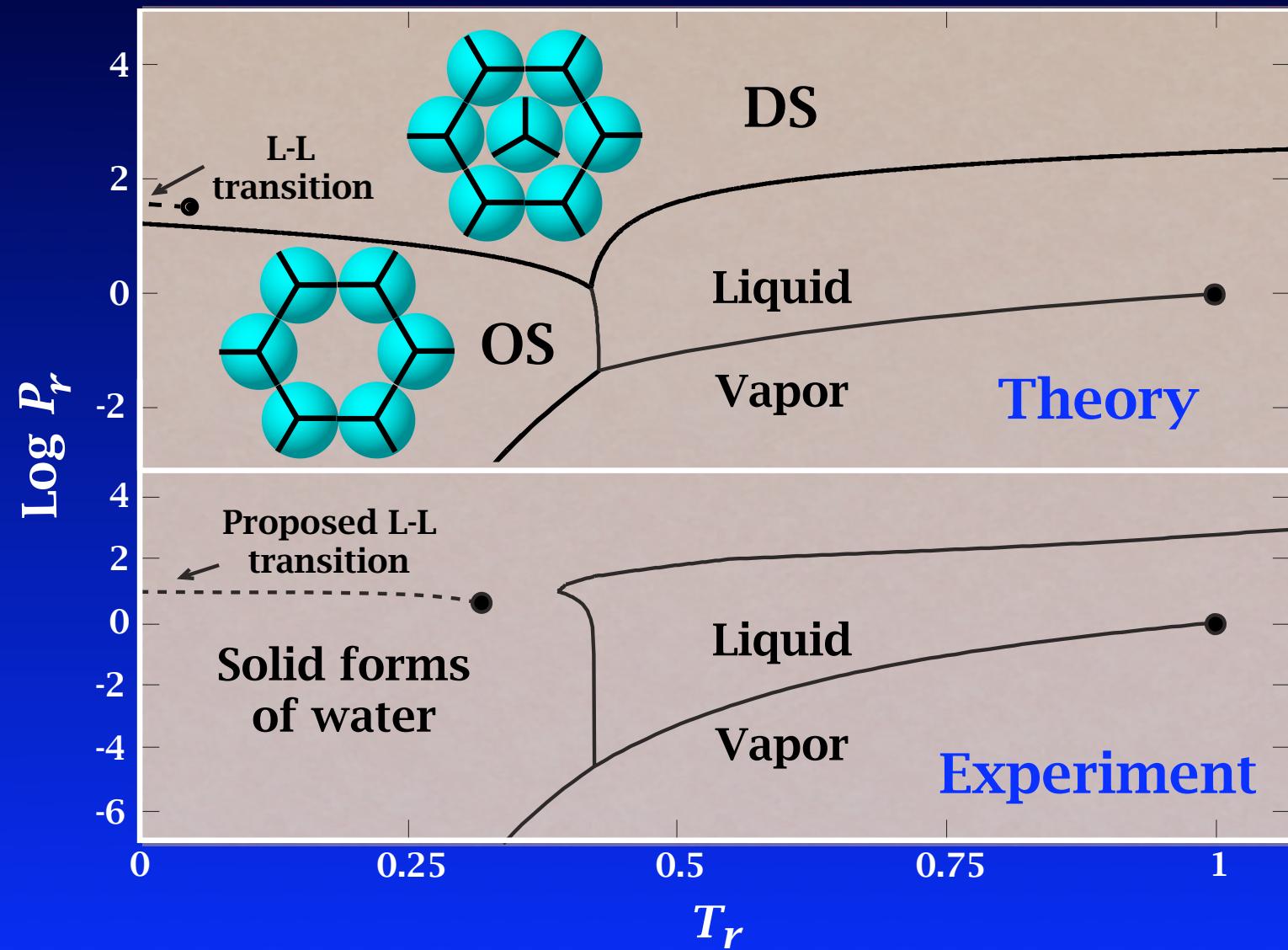
$$g_3 \alpha_3 = (kT/pd^2) e^{\{-1+[p(2+\sqrt{3})d^2]/(4kT)\}}$$

$$\mu = -(kT/N) \ln \Delta \quad \quad \quad \nu(T, P) = -(\partial \mu / \partial p)_T$$

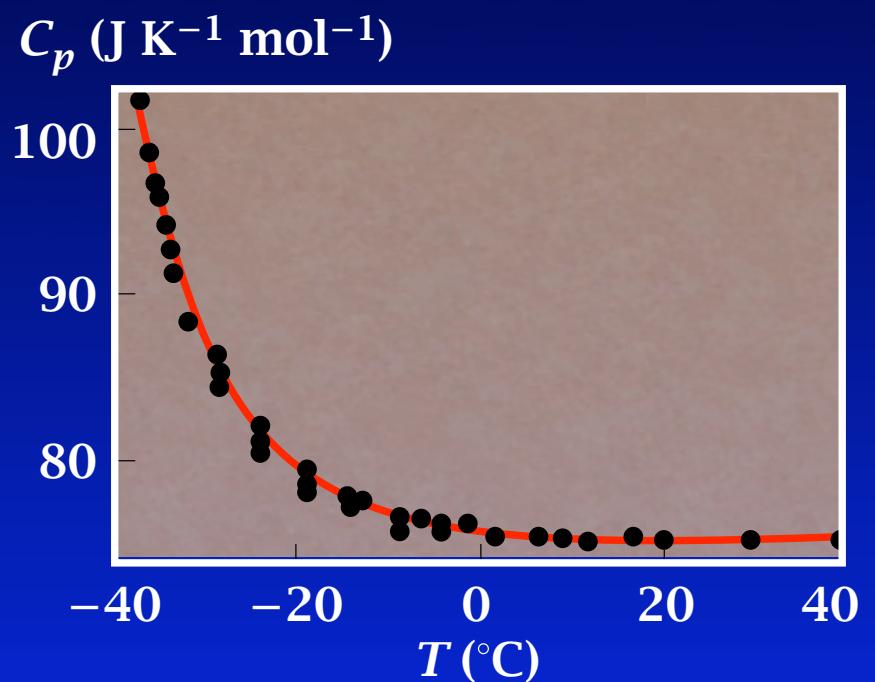
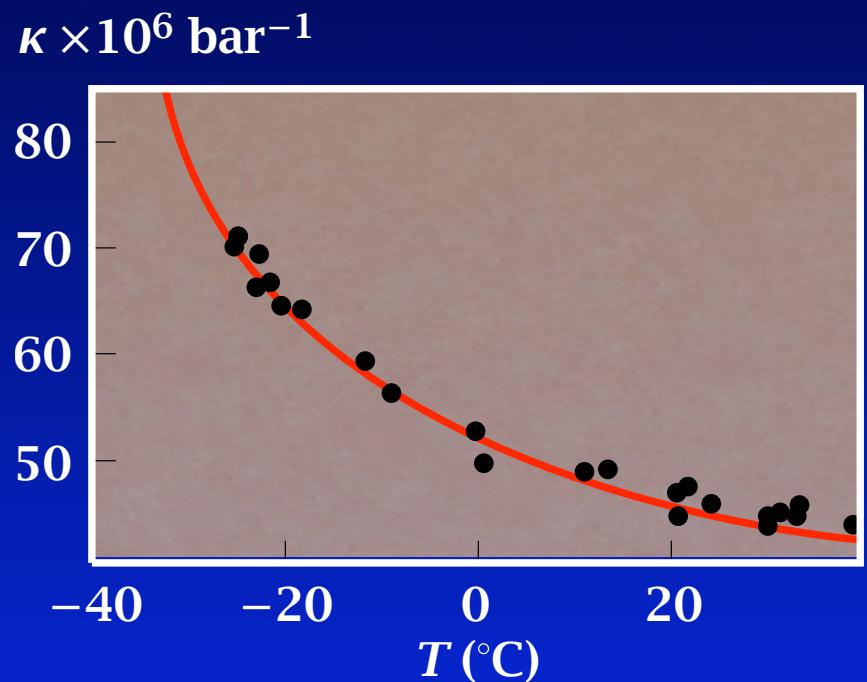
Anomalous Thermodynamics of Water



Phase Diagram of Water

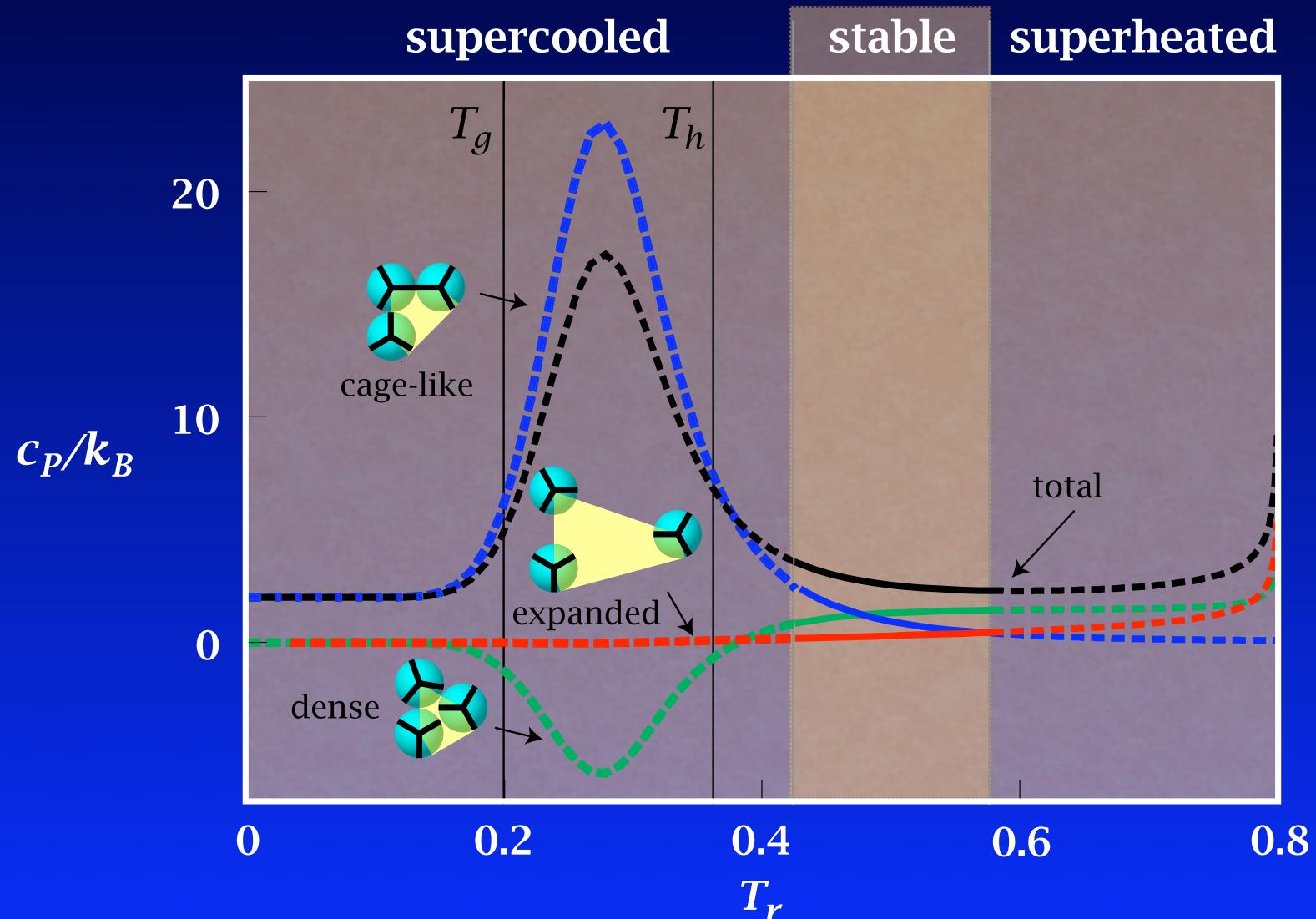


A Phase Transition in Supercooled Water



PG DeBenedetti, Metastable Liquids, Concepts and Principles, 1996

Supercool Transition: Melting Cages to Dense Liquid



Thanks To:

Kevin Silverstein

Tom Truskett

Barbara Hribar-Lee

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Tomaz Urbic

Vojko Vlachy

www.dillgroup.ucsf.edu

Silverstein et al, JACS 120: 3166 (1998)

Southall & K Dill, J Phys Chem 104: 1326 (2000)

Hribar et al, JACS 124: 12302 (2002)

Truskett and Dill, J Phys Chem B 106, 11829 (2002)

Dill et al, Ann Rev Biophys Biomol Struc, 34, 173 (2005)